Electrochemical dehydrodimerisation of a vinylenylamide ligand: formation of the binuclear group {Mo≡N$^+$CH=CHCH=CHCH=CHN$^+$≡Mo} which displays very strong electronic coupling in the {(Mo$^{\mathrm{III}}$)–(Mo$^{\mathrm{IV}}$)} mixed-valence state

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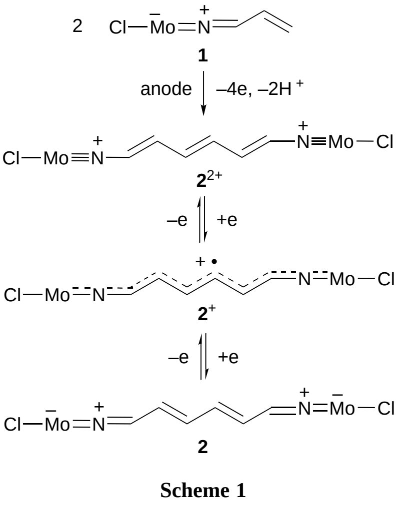
Electrochemical dehydrodimerisation of an {Mo–N=CHCH=CH$_2$} group gives an all-*trans*-{≡N$^+$CH=CHCH=CHCH=CHN$^+$≡} ligand, bridging two Mo$^{\mathrm{IV}}$ centres; the {(Mo$^{\mathrm{III}}$)–bridge–(Mo$^{\mathrm{IV}}$)} mixed-valence state is accessible by electrochemical reduction and exhibits very strong electronic coupling over the 11.7 Å which separates the two metal centres; this accords with EHMO calculations which show that the SOMO has substantial (30%) bridging-ligand character; in its capacity to function as a molecular wire linking two metal centres, the eight-atom hexatriene di(imide) chain {N(CH)$_6$N} compares favourably with C$_8$ chains of acetylenic carbons bridging other metal centres.

An extensive and diverse chemistry of enylamide ligands (–N=CR$_2$; R = H or organic group) is developing, particularly at molybdenum(II) centres.[1] For example, recently it has been shown that incipient carbanionic character at the γ-carbon atom within the {Mo–N=CHCH=CH$_2$} group allows regio- and stereo-specific addition of carbon electrophiles.[2] We now report a new reaction of this vinylenylamide group: anodic dehydrodimerisation to give the hitherto unknown {≡N$^+$CH=CHCH=CHCH=CHN$^+$≡} bridging ligand.

Controlled potential oxidation of *trans*-[MoCl(N=CHCH=CH$_2$)(dppe)$_2$] **1** {dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; vitreous carbon; -0.55 V *vs.* ferrocenium–ferrocene (Fc$^+$–Fc); 0.2 M [NBu$_4$][BF$_4$] in tetrahydrofuran(thf)–KOBu^t (2 equiv.)} gives all-*trans*-[Cl(dppe)$_2$Mo≡NCH=CHCH=CHCH=CHN≡MoCl(dppe)$_2$]$^{2+}$ **2**$^{2+}$ in an overall two-electron process, Scheme 1.

Cation **2**$^{2+}$ is formed in *ca.* 70% yield and was isolated from the anolyte as the tetrafluoroborate salt. Recrystallisation from CH$_2$Cl$_2$–EtO$_2$ gave **2**[BF$_4$]$_2$·solvent as dark-orange plates and the structure was determined by X-ray crystallography.‡ This established that the alternate-hydrocarbon bridge has the all-*trans* arrangement as shown in Fig. 1. The *trans*-Cl–Mo–N arrangement at each Mo atom, and the dimensions about the metal atoms, are similar to those found in the molybdenum(IV) methylimide cation *trans*-[MoCl(NMe)(dppe)$_2$]$^+$ **3**$^+$.[3]



Scheme 1

The bridging ligand, which places the two Mo atoms 11.7 Å apart, is unique in that a polyene unit is linked to the metal centres by multiply bonding imide groups. The electronic consequences of this arrangement are considerable. EHMO calcualtions[4] indicate that the LUMO of **2**$^{2+}$ has both metal (30%, 30%) and bridging-ligand π*-character (30%).§ Populating this delocalised orbital by one-electron reduction leads to strong electronic coupling between the metal centres in the mixed-valence ion **2**$^+$ (Robin and Day, Class III behaviour[5]) as is borne out by the following experimental evidence.

Cyclic voltammetry {vitreous carbon; 0.2 M [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$} shows that **2**$^{2+}$ undergoes two successive reversible one-electron reductions with $\Delta E° = 320$ mV ($K_{\mathrm{com}} = 2.6 \times 10^5$) which is indicative of Class II or Class III behaviour, Fig. 2.

Controlled potential electrolysis {vitreous carbon; -1.35 V *vs.* Fc$^+$–Fc; 0.2 M [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$} cleanly generates **2**$^+$ as a stable, paramagnetic solution species ($S = 1/2$; $g_\perp = 1.998$, $g_\parallel = 1.960$; frozen glass, 77 K). The electronic spectrum of electrogenerated **2**$^+$ shows an intense symmetric intervalence charge-transfer (IT) band in the near-IR at 12 820 cm^{-1} which is absent in **2**$^{2+}$.

The IT band-width at half-peak intensity ($\Delta\nu_{1/2}$) can be calculated for Class II systems from $\nu_{\max}$ using the Hush equation.[6] This gives $\Delta\nu_{1/2}$ (calc.) = 5442 cm^{-1} whereas $\Delta\nu_{1/2}$ (exptl.) = 702 cm^{-1}: IT bands which are considerably sharper than predicted typify Class III character. The intensity of IT bands in Class II complexes are weak with $\varepsilon_{\max}$ typically in the order of 10^2 dm^3 mol^{-1} cm^{-1}; in addition $\nu_{\max}$ is solvent dependent. In contrast, Class III complexes display intense solvent-independent IT bands. **2**$^+$ has $\varepsilon_{\max} = 9.5 \times 10^4$

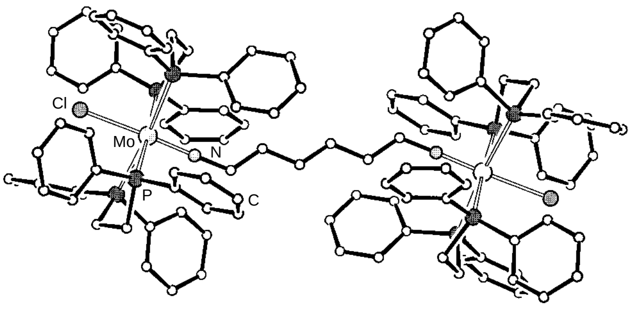


Fig. 1 View of cation [{MoCl(dppe)$_2$}$_2${μ-N(CH=CH–)$_3$N}]$^{2+}$; the two halves are related by a centre of symmetry. Selected molecular dimensions: Mo–Cl 2.521(4), Mo–N 1.752(11), mean Mo–P 2.551(7) Å; Mo–N–C 178.0(10)°.

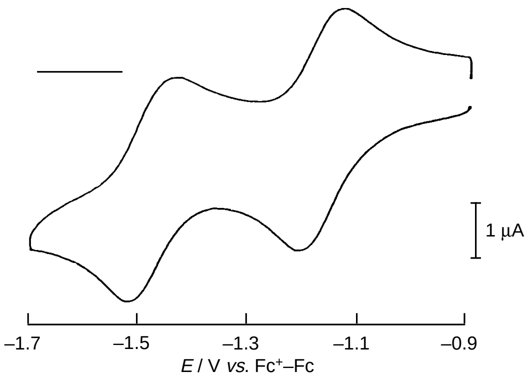


Fig. 2 Cyclic voltammogram at 293 K of $\mathbf{2}^{2+}$ at vitreous carbon electrode in 0.2 M $[NBu_4][BF_4]$–CH_2Cl_2 at a scan rate of 30 mV s^{-1} showing two successive reversible one-electron reductions. Electrode area = 0.0707 cm^2; concentration of complex = 0.26 mM.

dm^3 mol^{-1} cm^{-1} and ν_{max} is solvent independent, again consistent with Class III assignment.

The crystallographic distance between the metal centres, ν_{max} and $\Delta\nu_{1/2}$ can be used to estimate the degree of delocalisation (α^2) in the ground state of a mixed-valence system.[6] For $\mathbf{2}^{+}$, α^2 is 0.25 which compares favourably with $\alpha^2 = 0.26$ for the Class III system $[(\eta^5\text{-}C_5Me_5)(dppe)Fe{-}C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C{-}Fe(\eta^5\text{-}C_5Me_5)(dppe)]^+$; this cation also has eight atoms separating the metal centres which are described as functioning as a 'molecular wire'.[7]

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Notes and References

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‡ Crystal structure analysis of $[\{MoCl(dppe)_2\}_2\{\mu\text{-}N(CH{=}CH{-})_3N\}][BF_4]_2{\cdot}nCH_2Cl_2{\cdot}mEt_2O$.

Crystal data: $C_{110}H_{102}B_2Cl_2F_8Mo_2N_2P_8{\cdot}CH_2Cl_2{\cdot}C_4H_{10}O$, assuming *n* and *m* are each 1.0, $M = 2295.3$, triclinic, space group $B\bar{1}$ (equiv. to no. 2), $a = 12.533(1)$, $b = 14.733(2)$, $c = 30.206(3)$ Å, $\alpha = 83.818(8)$, $\beta = 94.801(8)$, $\gamma = 83.150(8)°$, $U = 5479.0(9)$ Å^3. $Z = 2$, $D_c = 1.391$ g cm^{-3}, $F(000) = 2360$, $T = 293$ K, μ(Mo-Kα) = 5.1 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Air-sensitive, thin, deep orange plate crystals. Preliminary photographic examination, then Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for accurate cell parameters (25 reflections, $\theta = 10–11°$) and diffraction intensities (5094 unique intensities (5094 unique reflections to $\theta_{max} = 20°$; 2643 'observed' with $I > 2\sigma_I$).

Corrections applied for Lorentz-polarisation effects, crystal deterioration (*ca.* 14.3% overall), absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). Structure determined by automated Patterson routines; refinement by full-matrix least-squares methods, on F^2 values, in SHELXL.[8] In the cation, non-hydrogen atoms refined anisotropically, hydrogen atoms included with all parameters riding. Anion and solvent regions show disorder and not fully resolved. At conclusion of refinement, $wR_2 = 0.182$ and $R_1 = 0.101$[8] for 3881 reflections (with $I > \sigma_I$) weighted $w = [\sigma^2(F_o^2) + (0.0964P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data, $R_I = 0.068$. In the final difference map, the highest peaks (*ca.* 0.67 e Å^{-3}) were close to the Mo centres. CCDC 182/766.

§ EHMO calculations[4] reveal that in $\mathbf{2}^{2+}$ a degenerate pair of occupied orbitals constitute two metal-based HOMOs each with 93% Mo character. Consistent with this, cyclic voltammetry (vitreous carbon; 0.2 M $[NBu_4][BF_4]$–CH_2Cl_2) shows that $\mathbf{2}^{2+}$ undergoes two successive and closely spaced ($\Delta E° = 100$ mV) reversible one-electron oxidations indicative of a valence-trapped $\{Mo^V(bridge)Mo^{IV}\}$ system.

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